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A comprehensive investigation on thermal stability of epoxy-TiO₂ nanocomposites

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ABSTRACT

Epoxy-TiO₂ nanocomposites' thermal stability was thoroughly examined throughout a wide range of nanoparticle loadings, ranging 0.5 wt% to 20 wt%. An optimized ultrasonic dualmixing technique ensured uniform distribution of titania nanoparticles within the viscous epoxy system. The study investigated how the glass transition temperature (T_g) and thermal stability of the nanocomposites are affected by inter-particle spacing and nanoparticle cluster size. Atomic force microscopy was used to characterize nanoparticle dispersion in epoxy. T_g was estimated using differential thermal analysis, and thermogravimetric analysis was employed to examine the thermal stability of the nanocomposites. It was found that a nanoparticle content around 10 wt% serves as a critical threshold for noticeable improvements in T_g and thermal stability. These enhancements are attributed to the formation of a robust epoxy-nanoparticle interface, driven by the even distribution of nanoparticles, it prevents the epoxy polymer chains from moving freely. Moreover, the nanoparticles' ceramic characteristics limit heat transfer through the matrix by acting as thermal insulators.

KEYWORDS: Epoxy; TiO₂; Glass transition temperature; Ultrasonic dual mixing; Thermal stability.

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1. Introduction

Epoxy is an important industrial material [1-9] with a variety of applications in the electronics, automotive, and aerospace

industries due to its exceptional stiffness and strength, minimal contraction while curing, chemical resistance,

outstanding corrosion resistance, as well as thermal characteristics. However, its applications are limited by other features such fragility, minimal resistance to crack propagation, and low wear resistance. To accomplish this, numerous studies have looked at different fillers which can be incorporated to improve the matrix's characteristics. An extensive variety of nano-fillers having different shapes, types, as well as characteristics have recently been investigated, like spherical nanoparticles [1], carbon nanotubes [2], nanoclays [3], graphenes [4] and MXenes [5]. One-dimensional and two-dimensional materials like carbon nanotubes, graphene, and MXenes, due to their high aspect ratio, have emerged as leading fillers for many polymers [5-7]. The high conductivity, however, restricts their use in applications requiring electrical insulation. Moreover, achieving uniform dispersion of such high-aspect-ratio nanomaterials in viscous polymers like epoxy is challenging. Additionally functional materials are required in such situation which makes the overall process complex and expensive, which is difficult to be adopted at industrial scale. Furthermore, these materials are toxic in nature which is another serious issue that restricts their usage in various fields. However, such issues are almost missing in case of ceramic nanoparticles such as titania, alumina, zirconia, etc. Such nanomaterials are quite cheap, available with an ease and less challenging for dispersion in viscous polymers because of their aspect ratio (~ 1) [8–10]. However, TiO₂ nanoparticles are recognized as the most preferable materials for reinforcing epoxy like polymers [11–13]. Strong van der Waals forces between nanoparticles often lead to agglomeration. Ultrasonic dual mixing has proven to be the most effective method for ensuring homogeneous dispersion of nanoparticles in viscous polymers like epoxy [14,15]. Incorporating TiO₂ nanofillers enhances both the glass transition temperature (T_g) as well as thermal stabilization of epoxy nanocomposites [16–19]. But, till date no systematic study has been performed on epoxy-TiO2 nanocomposites to evaluate their thermal stability.

In the current study, a systematic study including a wide range of nanoparticles from 0.5 wt% to 20 wt% into epoxy is performed to assess the thermal stability of epoxy-TiO₂ nanocomposites. An optimized ultrasonic dual mixing was employed to disperse nanoparticles in viscous epoxy.

2. Experimental

Loctite E60-HP based a two-component adhesive, composed of epoxy resin derived from diglycidyl ether of bisphenol-A and an aliphatic polyamine derived hardener was sourced from Loctite Hysol, USA. Methyl ethyl ketone (MEK) was acquired from Sigma Aldrich, India. TiO₂ nanoparticles, which have an average size of about 48 nm, were acquired from American Elements in the United States.

An optimized ultrasonic dual mixing (UDM) [15] was exploited to make epoxy-TiO₂ nanocomposites containing titania nanoparticle 0.5–20 wt%. The scheme of UDM process (Fig. 1) [10] and its optimized factors are reported in earlier published work [15]. In 3-fold volume of epoxy resin, MEK was blended to lower the epoxy resin's viscosity and to cool down the mixture. Using a four-bladed impeller, the epoxy resin and MEK mixture was completely mixed with the highest concentration of TiO₂ nanoparticles (20 wt%) for 0.5 h at a high-speed of 2000 rpm. Then, the blend was processed using optimized UDM consisting of impeller and ultrasonic vibrator (Vibracell ultrasonic processor, Sonics & Materials, Inc.) for 1 h. Later, from the mixture, MEK was removed by using evaporation and heating the mixture at 70 °C under high vacuum [10]. Aliphatic polyamine based curing agent (or hardener) was mixed to the nanoparticle containing epoxy resin as per the technical data sheet of the material supplier and blended using the impeller at very low speed of 300 rpm for short duration of 10 min followed by removing the air trapped in the mixture under high vacuum. Lastly, the material was cast into the petri dish having Teflon coating and cured for 24 h at ambient temperature. Thereafter, from the petri dish, the cured material extracted and cleaned using acetone before its characterization.



Fig. 1. Scheme of UDM process for epoxy nano-composite (10,15).

With the use of an AFM (NT-MDT, Ntegra) tapping mode atomic force microscope, the morphology of cured epoxy nanocomposites was analyzed. The nanoparticle distribution and their cluster size in epoxy matrix was analysed using AFM images of the nanocomposites followed by their image analysis using Image software [10]. The nanocomposites from the bulk samples were cut down to small pieces of \sim 3 mm to characterize using differential thermal analyser (DTA) and thermo-gravimetric analyser (TGA) (Perkin Elmer, Pyris Diamond). N2 purging gas flow at rate of 200 ml/min was used to heat each specimen, which weighed around 20 mg, between 30 °C and 700 °C at a rate of 10 °C/min. The ASTM E1356 standard [10] was followed in measuring the glass transition temperature (Tg) from DTA analysis, and the TGA thermograms were used to estimate the thermal stability. For the DTA tests, a heating rate of 10

 $^{\circ}$ C/min and an operating temperature range of 30 to 300 $^{\circ}$ C with N₂ purging gas were used. For every composition, at least 3 repetition tests were conducted, and the mean values together with the standard deviation are presented. A 20 mg weight sample of highly pure alumina powder was employed as the reference material for thermal measurements.

3. Results and Discussion

3.1. Morphology of nanocomposites

AFM images of Epoxy-TiO₂ (5 wt%) and Epoxy-TiO₂ (10 nanocomposite (Fig. 2) revealed individual wt%) nanoparticles (highlighted by solid circles), cluster of few nanoparticles (highlighted by dotted circles) and presence of some cavities. Majority of the particles are distributed evenly into the epoxy polymer; however, cluster of some nanoparticles are present in both the nanocomposites. But further increase of nanoparticle concentration in epoxy like 15 wt% and 20 wt% leads to significant clustering [15]. Thus, the threshold limit for effective nanoparticle dispersion into the epoxy is 10 wt%. This indicates, the optimized UDM generates enough energy for the dispersion of nanoparticles up to their individual level into the epoxy. But, for further effective distribution of large content of particles up to 20 wt%, there is a need to optimize the process parameters of UDM technique. Fig. 3 displays the concentration of nanoparticles versus average cluster size. A little increase in cluster size occurs when epoxy contains nanoparticles at concentrations between 0.5 wt% and 3 wt%. However, for nanoparticle concentrations up to 10 wt%, a twofold increase in cluster size (close to 100 nm) is seen. The size of the cluster increases significantly with additional increases in nanoparticle concentration. **Fig. 4** displays the nanoparticle content versus average inter-particle distance based on theoretical calculations and experimental data. Equation (1) was utilized to estimate theoretical inter-particle distance. The cubic distribution of particles in a polymer is considered in the equation. Equation 1 provides the relationship between the filler content (φ) and the inter-particle distance (τ) [15].

$$\tau = d \left[\left(\frac{\pi}{6\varphi}\right)^{1/3} - 1 \right] \tag{1}$$

where d is the particle's diameter, φ is the filler content, and τ is the inter-particle spacing. The theoretical value is slightly less than the experimentally measured value for interparticle distance because of the presence of some form of clusters of nanoparticles for each concentration. As epoxy's nanoparticle concentration rises, the spacing between particles decreases. Less than 100 nm distance between the particles at the threshold limit of nanoparticles (10 wt%) in epoxy, which restricts the movement of the polymer chain and, as a result, greatly influences the thermal characteristics of the nanocomposites.



Fig. 2. AFM pictures of (a) epoxy-TiO₂ (5 wt%) and (b) epoxy-TiO₂ (10 wt%) nanocomposites.



Fig. 3. Nanoparticle content versus average cluster size of Epoxy-TiO₂ nanocomposites (15).



Fig. 4. Nanoparticle content versus average interparticle distance of epoxy-TiO₂ nanocomposites (15).

3.2. T_s of nanocomposites

Fig. 5 displays the TiO₂ content versus T_g of epoxy nanocomposites with standard deviation. The T_g of the epoxy nanocomposites almost linearly increases up to the threshold limit (10 wt%) of nanoparticles thereafter it shows a decline. A noteworthy enhancement (~ 54%) in T_g of the nanocomposite is achieved compared to the neat epoxy [15]. The enhancement in T_g is due to the restriction of polymer

chain movement because of change in the local structure of nanoparticle dispersed epoxy [20]. The highly dispersed nanoparticles are making a good interface with the epoxy polymer. In contrast to previous results [21–23], the nanocomposite exhibits a significantly larger boost in Tg. The considerable clustering of nanoparticles, however, reduces the particle-polymer contact and lowers the T_g value beyond the threshold limit. To learn more about the effects of nanoparticle cluster size on the T_g value, a graph is plotted between cluster size and Tg of the nanocomposites as shown in Fig. 6. The T_g continues to rise dramatically with the expansion of the clusters from 48 to 103 nm (containing ~ 2 nanoparticles) but beyond this limit a decline in the T_g has been realized for increasing cluster size from 157 to 245 nm. A second order polynomial relation is found as $T_g =$ $-0.002 x^2 + 0.596 x - 54.995$ with the correlation factor, $R^2 = 0.639$, indicating a good relation between T_g and cluster size. Additionally, it has been observed that the Tg of the nanocomposites depends on three factors such as dispersion quality, nanoparticle content and cluster size. When 10 wt% TiO₂ nanoparticles are added to epoxy, the T_g of the resultant nanocomposite is greatly enhanced. The decrease in chain segment mobility of epoxy polymer because of nanoparticle-matrix interaction is responsible for the rise in T_g of the resultant nanocomposites. Because they can function as physical crosslinkers by raising the apparent crosslink density, nanoparticles limit the mobility of the polymer chain and improve the cross-linking action. However, because of nanoparticle agglomeration, the T_g decreases when the nanoparticle content increases over the threshold limit of 10 wt%. The obstacle provided by the numerous clustered nanoparticles to the base matrix's crosslinking density may be the cause of the T_g's decline.



Fig. 5. Nanoparticle content versus T_g of epoxy-TiO₂ nanocomposites (15).



Fig. 6. Effect of cluster size (x) on $T_{\rm g}$ of epoxy-TiO_2 nanocomposites.

3.3. Thermal stability of nanocomposites

Fig. 7 displays TGA graphs of pristine epoxy and nanocomposites for weight losses up to 50%. Table 1 shows the values of the thermal decomposition temperature (Td) for nanocomposites at various weight loss percentages.



Fig. 7. TGA curves displaying the weight remaining percentage of epoxy-TiO₂ nanocomposites versus temperature.

Because most researchers view 50% weight loss as a sign of structural instability, this percentage of total weight loss is used in this work to determine the nanocomposites' structural destabilization point [24].

	Thermal decomposition temperature (T _d) $^{\circ}$ C									
Weight Remaining (%)	Neat	Epoxy-TiO₂ nanocomposites containing nanoparticle (wt%)								
	Ероху	0.5	1	2	з	5	7	10	15	20
90	307	312	314	322	323	337	353	363	332	316
80	333	336	337	346	349	358	369	383	356	342
70	347	349	351	358	363	373	384	397	369	355
50	375	383	384	393	399	418	422	431	409	382
Char yield % at 700 °C	9.75	9.92	10.98	12.08	13.12	14.97	16.35	18.71	20.33	23.05

Table 1. TGA results for epoxy- TiO₂ nanocomposites and neat epoxy.

Fig. 8 displays the variance in weight loss percentage versus T_d for both neat epoxy as well as nanocomposites. The T_d of the epoxy nanocomposite, which contains 10 weight percent TiO₂ nanoparticles, is determined to be 363 °C for a 10% weight loss, while the neat epoxy's T_d is 307 °C for the same percentage of weight loss. The T_d of the epoxy nanocomposite (including 10 weight percent TiO₂ nanoparticles) is determined to be 431 °C, compared to 375 °C for the neat epoxy at 50% weight loss of the material. Therefore, as

compared to pristine epoxy, there is an increment in thermal stability of epoxy nanocomposite as the nanoparticle concentration rises from 0.5 to 10 weight percent. However, it then sharply declines at 20 weight percent of nanoparticle content. According to **Table 1**, the neat epoxy's TGA curve yielded a char yield percentage of almost 9.75 at 700 °C. The epoxy nanocomposites' TGA curves with embedded 20 wt% of particles show that the maximum values of char yield percent at 700 °C is 23.05. Because ceramic nanoparticles

(TiO₂) are present, it is evident that as the nanoparticle concentration increases from 0.5 to 20 wt%, the char yield percentage increases monotonically.



Fig. 8. Weight loss % versus $T_{\rm d}$ of neat epoxy and epoxy-TiO_2 nanocomposites.

to understand the degradation Prior of epoxy nanocomposites, the degradation of aliphatic polyamine cured epoxy network (which is used as the base matrix in the present work) need to be understood. The cured epoxy resin network typically undergoes a two-stage breakdown process. The evaporation of leftover solvent and adsorbed humidity is responsible for the first stage, which happens at a temperature of 35 to 310 °C [25]. The 2nd step appears from 310 °C to 450 °C because of the heat decomposition of the cured epoxy network. Dehydration, which results in the removal of water molecules from the oxypropylene group (-CH₂-CH(OH)-), causes the aliphatic polyamine-cured epoxy network to degrade. This occurs concurrently with the breakdown of the epoxy network and the subsequent creation of double bonds [25]. And the scission of (CH-CH₂) and (O-CH₂) bonds proceeds in parallel. The degradation causes product formation in terms of unsaturated phenolic compounds, which either polymerize to form char or released as gaseous products [25].

Thus, the degradation of epoxy nanocomposites also exhibits a two-stage process as reflected from TGA thermograms (**Fig. 7**). Because TiO₂ nanoparticles are ceramic, when they disperse uniformly, they create a barrier to heat transfer through the epoxy [24,26,27]. The number of nanoparticles increases the resulting nanocomposites' ability to withstand heat, because the quantity of particles increases. The supremacy of particle-to-particle over particle-topolymer interface occurs, however, when the particle content is raised above 10 wt%. Therefore, the cross-linking density is decreased by the rise in particle concentration and notable clustering (**Fig. 3**). As a result of their often-high crosslinking densities, thermosetting polymers have high breakdown temperatures [28]. When the epoxy matrix's whole stoichiometry is preserved, the cross-linking density is maximized. The addition of foreign particles (TiO₂) above a critical limit will cause the epoxy matrix's stoichiometry to fail [28], which will reduce the crosslink density and lower the decomposition temperature. Therefore, when the nanoparticle content exceeds the threshold limit, a decreased decomposition temperature is seen. Because of the ceramic nature of the particles, epoxy nanocomposites with nanoparticle contents over their threshold limit (10 wt%) exhibit less heat retardant effect, resulting in reduced thermal stability.

3.4. Thermal degradation kinetics of nano-composites

The kinetic study offers specific details on the polymer breakdown mechanism as well as hints regarding the process's energy barriers. To obtain information on the kinetics of epoxy composites' thermal degradation, the wellknown Coats Redfern model (CR) [29] and integral model of Horowitz and Metzger (HM) [30] have been used in this work. Several techniques can be used to derive kinetic information from dynamic experiments. The CR plots of plain epoxy and epoxy nanocomposite treated with one order reaction are displayed in **Fig. 9**. The Horowitz and Metzger plots of neat epoxy and epoxy composite are displayed in **Fig. 10**. Whereas, **Fig. 11** displays the E_a of neat epoxy and epoxy composites, which were determined using CR and HM plots.



Fig. 9. The Coats Redfern method-based heat degradation kinetics of neat epoxy and epoxy- TiO_2 (10 wt%) nanocomposite.

With both the CR and HM techniques, E_a of decomposition of epoxy-TiO₂ nanocomposites reduces with increased nanoparticle content from 10–20 wt% and raises with the surge in TiO₂ from 0.5–10 wt%. The E_a determined using CR

method shows a maximum value of ~146 kJ/mol for threshold nanoparticle content (10 wt%). But the activation energy calculated using HM method for the same nanocomposite shows a maximum value of ~ 161 kJ/mol. Thus, the loading of TiO₂ nanoparticles in epoxy results in noteworthy rise in the E_a of decomposition of the resulting nanocomposite, which is responsible for enhanced thermal stability of the nanocomposite.



Fig. 10. Horowitz–Metzger method-based heat degradation kinetics of neat epoxy and epoxy- TiO_2 (10 wt%) nanocomposite.



Fig. 11. CR and HM methods-based E_a of decomposition of the neat epoxy and epoxy-TiO₂ nanocomposites.

 E_a of decomposition also follows the same trend as thermal stability for epoxy nanocomposites. The highest improvement in the E_a of decomposition of epoxy-TiO₂ (10 wt%) nanocomposite is about 86% using CR method and

74% using HM method if compared with neat epoxy. The difference in the activation energy of decomposition for HM and CR methods for a particular nanocomposite is due to the use of different kinetic equations. The observed rise in the activation energy during the decomposition of nanocomposites could potentially be attributed to successful structural evolution, particularly in the context of homogeneous nanoparticle dispersion within the epoxy matrix. The ceramic nature of the nanoparticles may be responsible for the increase in activation energy. This is because the nanoparticles limit the molecular motion of polymer chain segments, which is reflected in improved Tg. Additionally, by limiting the flow of heat in the epoxy resin, they can create a barrier to random scission epoxy network formation. In the event of uniformly distributed nanoparticles within the matrix, the pathway leading to random molecular scission is exacerbated. Because the increase in the number of obstacles to the heat flow through the matrix. However, accumulation of nanoparticles and their uneven dispersal within the epoxy, which makes them less efficient at blocking heat, have a negative impact on the activation energy of breakdown when the quantity of particles in epoxy is increased beyond 10 wt%.

3.5. Integral procedural decomposition temperature (IPDT)

Using IPDT established on Doyle's method [31], the thermal stability of the neat epoxy as well as epoxy-TiO₂ nanocomposite was further assessed. Detailed instructions for determining IPDT are available in the literature [10]. IPDT, which encompasses the whole spectrum of stability, is calculated using TGA thermograms in three stages: first disintegration, rapid disintegration, and the last step of char formation. Fig. 12 displays the IPDT of the neat epoxy and epoxy composites. For neat epoxy, the IPDT calculated using TGA curves is around 398.48 °C. Nonetheless, the IPDT continues to rise as the nanoparticle concentration rises from 0.5 to 20 weight percent. the highest number of nanoparticles (20 wt%) gives the maximum value of IPDT. The maximum value of IPDT for epoxy nanocomposite is 564.61. Therefore, when compared to neat epoxy, the epoxy exhibits noticeably higher thermal resistance due to the addition of oxide nanoparticles. In every instance, it is found that the pattern of IPDT modification with increasing particle concentration differs from the pattern noted for Ea. It is most likely caused by the physical differences between the IPDT and the E_a of decomposition [32]. The E_a of decomposition considers only fast decomposition, neglecting the other two components, whereas the IPDT reflects the specimen's overall stability throughout the course of three stages: initial breakdown, quick decomposition, and the final phase of char formation. The increase in IPDT with the increase in particle content is due to the increase in char content with increasing particle content. The reason behind the rise in IPDT as particle

content increases is the corresponding rise in char content. When the nanoparticle loading in the epoxy matrix increases, the char yield percentage rises as well (**Table 1**), peaking at 20 weight percent. As a result, up to 20 weight percent of nanoparticle loading, the IPDT of epoxy nanocomposites increases monotonically.



Fig. 12. Nanoparticle content versus IPDT of epoxy-TiO_nanocomposite.

4. Conclusions

Epoxy-TiO₂ nanocomposites were synthesized using an optimized UDM method. A threshold limit of around 10 wt% TiO2 nanoparticles with a cluster size of 103 nm and an interparticle spacing of roughly 96 nm was determined. The T_g value and thermal stability of the nanocomposite were found to be significantly enhanced by approximately 54% at the threshold limit of nanoparticles. Because of the uniform distribution of the nanoparticles, the nanocomposite's increased Tg value and thermal stability are attributed to a strong matrix-particle contact. The decrease of chain segment mobility of the epoxy polymer because of the interaction between the nanoparticle and matrix was found responsible for the increase in Tg. By increasing the apparent crosslink density, nanoparticles can operate as physical cross-linkers, restricting the free motion of polymer chains and enhancing the cross-linking effect. The ceramic character of oxide nanoparticles, which function as insulators to the transport of heat through the matrix, may be responsible for the increase in thermal stability. The uniform dispersion of nanoparticles creates a multitude of barriers to the heat movement within the epoxy matrix.

Disclosure statement

The authors declare no relevant financial or non-financial interests.

Data availability

Raw data of the research article is available with the authors and will be provided as per a request from the journal.

Ethical approval

Not applicable.

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